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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

A REVISION OF THE ATOMIC WEIGHT OF IRON. — PRELIMINARY PAPER.

By Theodore William Richards and Gregory Paul Baxter.

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It is rather surprising that the atomic weight of a metal so important as iron should have received so little recent attention as it has. Berzelius* was among the first to determine the quantity under discussion; and in order to accomplish the determination he converted Swedish piano-wire into ferric oxide. For many years his very low result, 54.3, was almost unchallenged, when in 1843 Wackenroder called attention to the fact that in some early analyses of ferric oxide Stromeyer and he had found the substance to contain only 30.1 per cent of oxygen, corresponding to an atomic weight of nearly 56. This led immediately to several investigations by Svanberg and Norlin, Berzelius, and Erdmann and Marchand, whose individual results upon the same ratio varied from 55.81 to 56.23, showing without a doubt that the low value was incorrect, and settling the question with all the accuracy necessary in that day. Rivot in 1850 published two poor analyses which shed no further light upon the subject; and the more recent work of Dumas, who analyzed the chlorides of iron in 1859, was no more accurate than his similar work on other metals. Since that time no work on the atomic weight worthy of notice has appeared, so that our present knowledge depends upon data obtained over fifty years ago. In the intervening time Stas has taught the world accuracy in chemical analysis, and countless complications and sources of inaccuracy have been discovered which then were unsuspected. The variations of nearly 0.8 per cent in the best determinations (all depending upon the composition of ferric oxide), point with emphasis toward the necessity of a modern determination. Such questions as the possible presence of gases in the oxide, the possibility of incomplete reduction, and the danger of contamination from the containing vessels, should obviously receive attention.

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* The references to all the sources of information are to be found in the critical discussion at the close of this paper.

The balance and weights used in the present study were the same as those used in other recent determinations of atomic weights.* It is needless to state that the weights were carefully justified, and that all the usual precautions necessary to procure accuracy in such work were observed. All the weighings were reduced to the vacuum standard, and the values of the atomic weights refer to the universally accepted standard $O = 16.000$.

One of the most important steps in such an investigation is clearly the choice of the substance to be analyzed, and the choice usually requires a careful preliminary qualitative and quantitative study of many compounds of the element under consideration. This work occupied a number of weeks, and in the course of it we found that the preparation of either ferrous or ferric halides in a pure anhydrous state offered so many difficulties that as yet no satisfactory method for the purpose has been devised. Ferric oxide, on the other hand, can be obtained in a variety of ways, hence the choice of the early experimenters seems to have been a wise one. The first step in a systematic treatment of the subject is obviously a repetition of the discordant work of half a century ago, with especial reference to the possible errors noted above.

Owing to the fact that most oxides formed from nitrates are known to include considerable quantities of oxygen and nitrogen,† ignition of ferric nitrate as a means of obtaining ferric oxide was at first rejected, and ferric hydroxide was used instead. Very pure iron ribbon was dissolved in sulphuric acid, and the metal was then deposited electrolytically from an ammonic oxalate solution. After the film had been dissolved in the purest nitric acid, the carbon was removed by filtration, and the iron was precipitated as ferric hydrate by the addition of an excess of ammonia which had been distilled into pure water contained in a platinum dish. The precipitate was washed thoroughly, collected upon a pure washed filter paper, separated from the filter paper while moist, and finally dried in a platinum dish upon the steam bath. The lumps of dried hydrate were crushed in an agate mortar and finally ignited for several hours in a current of pure dry air. During the latter operation the weighed platinum boat with the oxide was contained in a large porcelain tube heated by a Fletcher furnace to about 900°. Constant weight within a few hundredths of a milligram was obtained without difficulty. The weighed oxide was then reduced in a current of electrolytic hydrogen which had been dried by means of fused potassic hydroxide. Ferric oxide is only very slowly reduced at the highest temperature which can be used with glass tubes, so that this reduction also was of necessity carried on in porcelain tubes. Even at about 900°,* long continued heating was needed to complete the reduction, the total period of ignition amounting sometimes to twenty hours. The progress of the reaction was slightly accelerated by alternate oxidation and reduction.

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* These Proceedings, **26**, 242 (1891).

† Richards, These Proceedings, **26**, 281 (1891). Richards and Rogers, ibid., **28**, 200.

Two analyses, carried out in the fashion described, are tabulated below. Corrections to a vacuum standard have been applied by adding 0.00009 gram to every apparent gram of ferric oxide, and 0.00001 gram to every apparent gram of metallic iron, the specific gravities of these two substances being assumed to be 5.2 and 7.9 respectively. †

SERIES I.

Number of Analysis.	Weight of Ferric Oxide in Vacuum.	Weight of Iron in Vacuum.	Atomic Weight of Iron.
1	3.17485	2.22096	55.885
2	3.61235	2.52750	55.916
		Average	55.900

The fact that both of these results are considerably lower than the accepted value of the atomic weight of iron (56.0) seemed to confirm a suspicion which had already arisen that ferric hydrate might not be completely converted into the oxide by ignition at a high temperature. That the oxide upon ignition easily reached constant weight is, however, evidence in the other direction. Since no direct method of proving the presence or absence of retained water was at hand, it seemed best to make use of another method of preparing ferric oxide. Although, as has been already stated, oxides formed from nitrates occlude nitrogen and oxygen, yet these gases are evolved upon solution of the oxides and can be determined. Ignition of ferric nitrate was therefore chosen as the next method of obtaining ferric oxide.

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* At the temperature to which the porcelain tubes were heated pure silver did not melt, while sodic chloride was easily fused.

† Landolt und Börnstein Tabellen, 118, 133 (1894).

The material used in the following work was purified with great care. In the first place a solution of a so-called "chemically pure" chloride of iron was treated with an excess of sulphuretted hydrogen and the resulting sulphides and sulphur were removed by filtration. From the filtrate, after oxidation with nitric acid, the iron was precipitated with an excess of ammonic hydrate and the precipitate was thoroughly washed by decantation. In this process traces of a number of metals which might have been present must have been removed. The precipitate was dissolved in sulphuric acid, and by cautious addition of ammonic hydrate basic ferric sulphate was thrown down; a precipitate which is much more easily washed than ferric hydrate, but which was redissolved in sulphuric acid with considerable difficulty. In order to reduce to the ferrous state the ferric sulphate thus formed, the solution was next subjected to the action of a galvanic current of several amperes. The solution was contained in a large platinum dish which served as the negative electrode, the positive electrode being a flat spiral of platinum wire. Since the solution was very concentrated and contained a considerable excess of sulphuric acid, the greater part of the ferrous sulphate crystallized out when the solution was allowed to cool. By alternately electrolyzing and cooling, almost all of the iron was eventually obtained as ferrous sulphate.

The next process in the purification was to deposit the iron electrolytically from a solution of its oxalate. By means of this separation, the aluminum and manganese could be eliminated, since the first, together with alkaline and other impurities, is not deposited by electrolysis, while the second is deposited upon the anode. The ammonic oxalate needed was prepared with great care. Oxalic acid which had been repeatedly crystallized with hydrochloric acid, and then until free from chlorine, was saturated with pure redistilled ammonia, and the resulting ammonic oxalate was subjected to several crystallizations. To a hot concentrated solution of this ammonic oxalate, the ferrous sulphate was added as long as no permanent precipitate resulted, and the solution was then electrolyzed until the greater part of the iron had been deposited. A slight deposit of hydrated manganese peroxide appeared upon the positive pole, which, however, presented enough surface to prevent the deposit from becoming detached. The film of iron was carefully washed and dissolved in pure dilute nitric acid. When all of the ferrous sulphate had been thus converted into ferric nitrate, the solution of the nitrate was filtered and evaporated, and the salt was three times recrystallized from a large amount of nitric acid. This acid had been distilled in a platinum still and condenser and collected in a platinum receiver. The mother liquor of the first crystallization was analyzed for impurities as follows: After precipitation of the iron as ferric hydrate by the addition of an excess of pure ammonia and filtration, the filtrate was evaporated to dryness and the residue was ignited. Since only a negligible amount of alkaline solid remained, it can fairly be assumed that the final preparation of ferric nitrate must have been free from such impurity. During the latter part of this purification platinum vessels only were employed, and the water and reagents were the purest obtainable.

The next step, that of converting the nitrate into oxide, was carried out in part by gentle heating in an electric oven at about 150°.* The resulting cake of basic nitrate, after removal from the platinum dish in which it was contained during the above operation, was crushed in an agate mortar, and the reaction was completed by ignition in an open porcelain tube at a temperature of about 900° for several hours. The oxide, which was now contained in a large platinum boat, was carefully weighed and again heated. The loss of weight during this second ignition amounted to one tenth of a milligram, while a third prolonged heating caused a further loss of three-tenths of a milligram. This difference must have been caused by the escape of included gases, and was so small in comparison with the weight of the oxide (seventeen grams), that further heating was deemed unnecessary.

The determination of the gases contained in this oxide proved to be a matter of considerable difficulty. At first the method used was that of dissolving the oxide in a Sprengel vacuum in fused acid potassic sulphate. Owing to the fact that the sulphuric acid, which was evolved from the fused sulphate, attacked both the rubber connections used for joining the apparatus, and also the stick potash used as a drying agent, it was uncertain whether the small quantity of gas which was collected in the air pump was originally included in the oxide. A more successful method was eventually found by dissolving the oxide in hot hydrochloric acid containing stannous chloride. The operation was carried on in an apparatus for determining the gases evolved during the solution of a substance, which has been already described in papers from this laboratory.† In two experiments half a gram of ferric oxide yielded a mere trace of gas. Cupric oxide treated in the same way evolved considerable gas, less, however, than that evolved when the same cupric oxide was dissolved in sulphuric acid. It was shown, however, that the gas which resulted upon solution in hydrochloric acid and stannous chloride consisted wholly of nitrogen, and that the volume of this nitrogen corresponded to the nitrogen in the gases set free by solution of the same oxide in sulphuric acid. Although it was evident that the oxygen was absorbed by the stannous chloride, yet, since in the case of all oxides heretofore examined the included gases consisted chiefly of nitrogen, it is fair to conclude that this was so in the case of ferric oxide. Only a trace even of nitrogen was evolved from the ferric oxide, hence this preparation must have been practically free from included gases.

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* Richards, Am. Chem. Jour., **22**, 45 (1899).

† These Proceedings, **28**, 200.

In order to avoid any error due to hygroscopicity, the oxide used for each analysis was bottled in dry air in the bottling apparatus, which has already been described elsewhere.* The platinum boat containing the oxide was heated in the hard glass tube while the air was exhausted from the apparatus by means of a Sprengel air pump. Dry air was then admitted, and the boat was pushed into the weighing bottle which was then stoppered and weighed with the usual precautions. Since in two instances repetition of the bottling failed to change the weight of the oxide, subsequently this precaution was omitted.

The oxide was then reduced in the manner already described, constant weight of the metal being attained much more easily than in the case of oxide prepared from ferric hydrate. Five closely agreeing results were obtained from analyses of material prepared as above.

SERIES II.

Number of Analysis.	Weight of Ferric Oxide in Vacuum.	Weight of Iron in Vacuum.	Atomic Weight of Iron.
3	3.97557	2.78115	55.883
4	4.89655	3.42558	55.891
5	4.35955	3.04990	55.891
6	7.14115	4.99533	55.870
7	6.42021	4.49130	55.882
		Average	55.883

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* These Proceedings, **32**, 59 (1896).

In order to determine if the reduction had been complete in the last two analyses of this series, the resulting metal was dissolved in cold dilute sulphuric acid. In each case a few tenths of a milligram of black insoluble matter remained, which contained platinum. This impurity probably came from the alloying of the boat with the iron during the reduction, and hence introduced no error. A trace of ferric oxide also was found. Even if the platinum had been originally present, the combined weight of the two impurities could not have raised the final result more than 0.01 per cent; hence no correction was applied.

One of us* has recently shown that iron when ignited at a high temperature, has practically no tendency to occlude hydrogen, so that in the present case this possible source of error is excluded. On comparing these results with the two determinations of the first series, one is forced to conclude that the oxide made from the nitrate has essentially the same composition as the oxide made from the hydroxide. The higher value indicated by Experiment 2, was probably caused by incomplete reduction, and the first experiment agrees with the average of the second series.

It is interesting to review the older determinations † in the light of the experience gained in these analyses. Evidently the occlusion (or better,

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* Baxter, Am. Chem. Journ., **22**, 363 (1899).

† A complete list of these determinations is given below : —

		Fe =
1814.	Wollaston, from Thenard's Results, Phil. Trans., **104**, 21 (1814)	55.2
1826.	Stromeyer, Pogg. Ann., **6**, 471 (1826). Reduction $Fe_2 O_3 : Fe$	55.5
1826.	Berzelius, Pogg. Ann., **8**, 185 (1826). Oxidation $Fe_2 : Fe_2 O_3$	54.3
1830±.	Wackenroder, Archive Pharm., **35**, 279; **36**, 22 (1843). Reduction $Fe_2 O_3 : Fe_2$	55.9
1844.	Svanberg and Norlin, Liebig's Ann. Chem. Pharm., **50**, 432 (1844), also Berzelius Jahresbericht, **24**, 121 (1845), and **25**, 42 (1846). Oxidation $Fe_2 : Fe_2 O_3$	55.87
	Reduction $Fe_2 O_3 : Fe_2$	56.09
1844.	Berzelius (the same references). Oxidation $Fe_2 : Fe_2 O_3$	56.02
1844.	Erdmann and Marchand, J. Pr. Ch., **33**, 1; Lieb. Ann., **52**, 212 (1845). Reduction of oxide from oxalate $Fe_2 O_3 : Fe_2$	56.02
1846.	Maumené, Ann. Chim. Phys. [3], **30**, 380 (1850). Oxidation $Fe_2 : Fe_2 O_3$	56.00
1850.	Rivot, Ann. Chim. Phys. [3], **30**, 192, (1850). Reduction $Fe_2 O_3 : Fe$	54.2
1859.	Dumas, Ann. Chim. Phys. [3], **55**, 157 (1859). Lieb. Ann., **113**, 26 (1860). Analysis of Chlorides	56.2

[The results of Magnus, Döbereiner, Capitaine (1841), and Torrey (1888), alluded to by Clarke, are not worthy of serious consideration. See Smithson. Misc. Coll.; Constants of Nature, **5**, 287 (1897); also **4**, 65 (Becker, 1880)].

From some of these values Clarke (1897) computed the value 56.021, while Messrs. Landolt, Ostwald, and Seubert [1898] chose the number 56.0.

inclusion) of gases by the oxide is a less serious cause of error in the case of iron than in most other cases, if the temperature of ignition is reasonably high. This is the chief probable error which would tend to make the results too low. The three most probable errors having the opposite effect are: — first, the possible presence of magnetic oxide in the ferric oxide; second, the possibility of incomplete reduction during the analysis of this substance; and third, the possible presence of alkaline, siliceous, or other non-reducible material. Wackenroder seems to have been the only experimenter who thought seriously of the first two of these errors; and none of the early experimenters paid any attention to the last, for until recently glass was supposed by most chemists to be wholly insoluble. Wackenroder's work was perhaps the most intelligently carried out of all the older determinations, although his individual analyses did not agree among themselves quite so well as some of the others. His greatest omission was the recognized lack of purity in his hydrogen, although he could not observe an error due to this cause. It is interesting to note that the average of his six results gives the value 55.82 for the atomic weight in question, while a corrected average obtained by rejecting the two most discordant values gives the value 55.92. The result of the present work indicates a value midway between the two averages. Wackenroder's valuable work does not enter into Clarke's average for the atomic weight of iron, for Clarke was unable to find the original paper.

In order to prepare pure iron for his later work, Berzelius fused his metal with ferrous oxide, but gave no proof of the effectiveness of his treatment. It is not impossible that traces of the oxide may have been held by the iron, as copper dissolves cuprous oxide. Erdmann and Marchand made the ferric oxide, which they reduced quantitatively, by the ignition of ferrous oxalate, — a method which invites the presence of magnetic oxide. Maumené's method was the process of filtration used in common analysis, in which the possible errors in both directions are plentiful.

These detailed criticisms, taken in connection with the general lack of accuracy which is to be observed in the quantitative work of half a century ago, seem to show that there is nothing improbable in the present result, 55.88. Of course the analysis of a single compound is never conclusive, so that this result is announced only as a preliminary one, which we shall hope to support or disprove in the near future.

HARVARD UNIVERSITY, Cambridge, Mass.,
October, 1899.